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Catalytic reduction of N_2O by CO on benzene clusters of Fe^+: Catalytic poisoning by CO

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Abstract

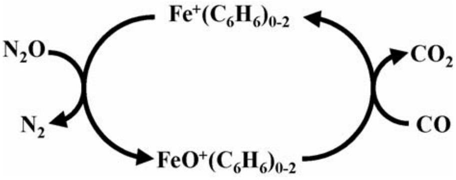
The catalytic reduction of N_2O by CO on ion clusters of Fe^+ and benzene was investigated using an ICP/SIFT tandem mass spectrometer. Both $Fe^+(C_6H_6)$ and $Fe^+(C_6H_6)_2$ are discovered to be effective in catalyzing the reduction of N_2O by CO. However, $Fe^+(C_6H_6)$ is found to be poisoned by CO in reactions forming $Fe^+(C_6H_6)CO$ and $Fe^+(C_6H_6)(CO)_2$. On the other hand, $Fe^+(C_6H_6)_2$ does not exhibit any poisoning by CO and so is the better catalyst. $FeO^+(C_6H_6)_{1,2}$ ions are observed as intermediates in the catalytic cycles. These results also provide the conceptual basis for a synthesis of CO_2 from CO and O atoms catalyzed by $Fe^+(C_6H_6)$ and related cluster ions in interstellar environments.

Keywords: Ion catalysis; Iron cations; Benzene; O-atom transport; N_2O reduction; CO poisoning

1. Introduction

Over the past few years mass spectrometric measurements in our laboratory have focussed on the role of bare atomic metal cations in the catalytic reduction of NO_x molecules by O-atom transport [1,2]. Also of particular interest were measurements of the reactivities of Fe^+ cations attached to benzene and coronene toward a variety of small inorganic and organic molecules [3]. The reactivity of the Fe^+ cation, a signature atomic ion in our studies of ion catalysis, was observed to be enhanced by attaching it to these and other carbonaceous ligands such as ethylene, cyclopentadiene, and C_{60} [4–8]. Reactions of Fe^+ attached to carbonaceous ligands are also of interest in the chemistry of dense interstellar clouds [9].

Here, we have investigated the effect of benzene on the catalytic O-atom transport by Fe^+ in the reduction of N_2O by CO (see Scheme 1). Ligation of Fe^+ with one and two molecules of benzene significantly alters the reactivity of Fe^+ with N_2O and CO and this, we shall see, has important consequences for the occurrence of catalytic poisoning by CO.



Scheme 1.

2. Experimental

The experiments were performed using the selected ion flow tube (SIFT) equipped with an inductively coupled plasma (ICP) ion source. Both the SIFT instrument [10] and its interface with the ICP ion source [11] have been described in detail elsewhere. Iron cations are formed in the ICP source, mass selected by a quadrupole mass filter and injected into the flow tube through a Venturi-type aspirator. The ions are then allowed to thermalize and ultimately react with selected neutral reagents. The reactant ion and any primary and higher-order product ions are analyzed by a second quadrupole mass filter.

In the experiments reported here both benzene and N_2O were added upstream into the flow tube, forming $FeO^+(C_6H_6)$ and $FeO^+(C_6H_6)_2$, which serve as the reagent cations in our study. The exact reaction sequence for the formation of these

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two cations is uncertain, since N_2O and benzene were added upstream together so that Fe^+ reacts effectively with a mixture of N_2O and benzene. The reaction of Fe^+ with N_2O [12] is much slower than its reaction with benzene [4], so it is far more likely that $FeO^+(C_6H_6)$ is formed by reaction of $Fe^+(C_6H_6)$ with N_2O rather than by reaction of FeO^+ with benzene. $FeO^+(C_6H_6)_2$ is likely to be formed by both the reaction of $FeO^+(C_6H_6)$ with benzene and the reaction of $Fe^+(C_6H_6)_2$ with N_2O. The reactions of $FeO^+(C_6H_6)$ and $FeO^+(C_6H_6)_2$ ions did not show the presence of states or multiple isomers with different reactivities and it is likely that both isomer-pure $FeO^+(C_6H_6)$ and $FeO^+(C_6H_6)_2$ are formed regardless of the actual reaction sequence leading to their formation. We have previously reported a 32% channel leading to $Fe^+(C_6H_6)N_2O$ in the reaction of $Fe^+(C_6H_6)$ with N_2O under similar operating conditions [4]. Our failure to observe $Fe^+(C_6H_6)N_2O$ in the experiments reported here implies that benzene can switch with N_2O to form $Fe^+(C_6H_6)_2$.

$FeO^+(C_6H_6)$ and $FeO^+(C_6H_6)_2$ are reacted with CO in the reaction region of the flow tube in the presence of both benzene and N_2O. Due to the cyclic nature of the reactions, the rate coefficients measured represent lower limits [2]. Unlike our previous studies in which a steady state analysis [2] could be performed in order to determine the rate coefficient of the reducing leg of the catalytic cycle, steady state analysis here did not provide any additional information. This is due to the complicated nature of the system in which, in addition to N_2O and CO, a third reagent, benzene, is involved, invalidating the assumptions used to derive the steady state equations.

3. Results and discussion

The reactions of $FeO^+(C_6H_6)$ and $FeO^+(C_6H_6)_2$ with CO were both investigated in the presence of N_2O in the flow tube. The reaction profiles are shown in Fig. 1. Both reactant ions exhibit the same primary oxide reduction, reaction (1a):

$$FeO^+(C_6H_6)_{1,2} + CO \rightarrow Fe^+(C_6H_6)_{1,2} + CO_2 \qquad (1a)$$

$$Fe^+(C_6H_6)_{1,2} + N_2O \rightarrow FeO^+(C_6H_6)_{1,2} + N_2 \qquad (1b)$$

The measured lower limits for the rate coefficients are $\geq 3.1 \times 10^{-11}\,cm^3\,molecule^{-1}\,s^{-1}$ for the reaction of $FeO^+(C_6H_6)$ and $\geq 1.3 \times 10^{-11}\,cm^3\,molecule^{-1}\,s^{-1}$ for the reaction of $FeO^+(C_6H_6)_2$. This compares with a value of $1.8 \times 10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$ for reaction (1a) with the bare iron oxide cation [2]. Reaction (1b) represents the oxidation leg of the catalytic cycle that has been observed in the absence of benzene to proceed with $k = 3.7 \times 10^{-11}\,cm^3\,molecule^{-1}$ [2]. We have reported previously that $Fe^+(C_6H_6)$ reacts with N_2O with $k = 3.3 \times 10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$ and 68% of the reaction proceeding by O-atom transfer [4].

The $Fe^+(C_6H_6)$ produced in reaction (1a) under the conditions of our experiment quickly reacts further with CO forming $Fe^+(C_6H_6)CO$ and $Fe^+(C_6H_6)(CO)_2$ by reactions (2a) and (2b) which effectively poison the $Fe^+(C_6H_6)$ catalyst by "finessing" the oxidation leg of the catalytic cycle, reaction (1b).

$$Fe^+(C_6H_6) + CO \rightarrow Fe^+(C_6H_6)CO \qquad (2a)$$

$$Fe^+(C_6H_6)CO + CO \rightarrow Fe^+(C_6H_6)(CO)_2 \qquad (2b)$$

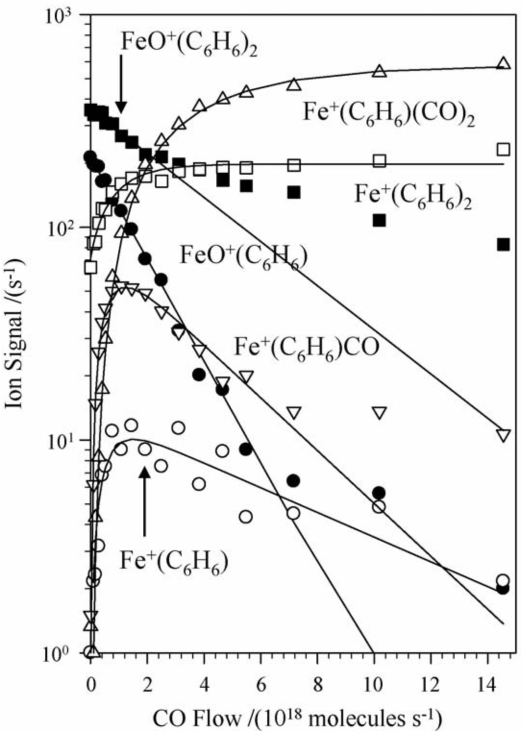

Fig. 1. Measured ion profiles showing reactions of $FeO^+(C_6H_6)$ and $FeO^+(C_6H_6)_2$ with CO. Both N_2O and benzene are present in the reaction region.

Previous SIFT measurements in our laboratory in which reactant Fe^+ ions were generated by electron impact of ferrocene provided effective bimolecular rate coefficients of 2.4×10^{-10} and $4.5 \times 10^{-11}\,cm^3\,molecule^{-1}\,s^{-1}$ for reactions (2a) and (2b), respectively [3].

$Fe^+(C_6H_6)_2$ on the other hand, is seen in Fig. 1 to undergo re-oxidation with the N_2O present in the flow tube and so to regenerate $FeO^+(C_6H_6)_2$ according to reaction (3a), rather than cluster with CO.

$$Fe^+(C_6H_6)_2 + N_2O \rightarrow FeO^+(C_6H_6)_2 + N_2 \qquad (3a)$$

$$FeO^+(C_6H_6)_2 + CO \rightarrow Fe^+(C_6H_6)_2 + CO_2 \qquad (3b)$$

$$FeO^+(C_6H_6)_2 + CO \rightarrow Fe^+(C_6H_6) + C_6H_6 + CO_2 \qquad (3b')$$

We note that reaction (3b) may be sufficiently exothermic to also promote the occurrence of channel (3b′) in which one of the benzene molecules is "boiled off". The failure of $Fe^+(C_6H_6)_2$ to cluster with CO likely is a consequence of the coordination of Fe^+ in $Fe^+(C_6H_6)_2$ which has 19 valence electrons (7 from Fe^+ and 12 from 2 benzene molecules). So coordination with CO to form $FeCO^+(C_6H_6)_2$ would be unfavorable (21 valence electrons) while formation of an Fe^+–O bond in $FeO^+(C_6H_6)_2$ (20 valence electrons) is preferred.

Most noticeable in Fig. 1 is the curvature in the decay of $FeO^+(C_6H_6)_2$ which is characteristic of the occurrence of a catalytic cycle, reactions (3a) and (3b). Such curvature is absent in $FeO^+(C_6H_6)$, except apparently at very low ion intensities that however can be attributed to a small background signal (a few cps).

Much more intriguing is the curvature exhibited by $Fe^+(C_6H_6)CO$, which may point to a novel catalytic cycle involving $Fe^+(C_6H_6)CO$ and $Fe^+(C_6H_6)(CO)_2$, reactions (4a) and (4b).

$$Fe^+(C_6H_6)(CO)_2 + N_2O \rightarrow Fe^+(C_6H_6)CO + N_2 + CO_2 \tag{4a}$$

$$Fe^+(C_6H_6)CO + CO \rightarrow Fe^+(C_6H_6)(CO)_2 \tag{4b}$$

In this cycle $Fe^+(C_6H_6)$ would be acting as a "true" catalyst, facilitating the reaction of N_2O with CO by activating one (or both) of the reagent molecules in an $[Fe^+(C_6H_6)(CO)_2(N_2O)]^*$ intermediate, rather than acting as an O-atom transporter. The net result is still the conversion of N_2O and CO to N_2 and CO_2. Several observations of such "bond activation catalysis" have been reported previously [13].

4. Conclusions

Our experiments have shown that the catalytic reduction of N_2O by CO by O-atom transport in the presence of an atomic-metal ion catalyst can be modified by the introduction of a third reagent, benzene. $Fe^+(C_6H_6)$ proved to be less suitable as a catalyst than the bare Fe^+ cation as it is quickly poisoned by CO, presumably due to the increased number of degrees of freedom and the binding energy with CO that are effective in enhancing the lifetime of the intermediate and so the rate of CO ligation. Also, $Fe^+(C_6H_6)_2$ has been shown to be quite efficient in the O-atom transport catalysis of the reduction of N_2O by CO. These results indicate an interesting variation of catalytic efficiency of Fe^+ with the degree of benzene ligation.

Very intriguing, and somewhat ironic, is the possibility that $Fe^+(C_6H_6)$ may act as a true catalyst after having been poisoned by CO as a catalytic O-atom transporter. The capture of N_2O by $Fe^+(C_6H_6)CO$ may foster sufficient activation of the attached N_2O and CO molecules to cause their mutual reaction and produce N_2 and CO_2. Such "bond activation catalysis" is known in analogous systems; this particular case resembles more closely heterogeneous catalysis.

Our results have implications for the possible occurrence of analogous catalysis in interstellar environments containing Fe^+ in the presence of benzene [14] or related PAHs or even fullerenes and carbonaceous grain particles. Attachment of Fe^+ to any of these carbonaceous species by radiative association followed by the capture of an O atom can set into motion catalytic cycles illustrated for benzene by reactions (5a) and (5b).

$$Fe^+(C_6H_6) + O \rightarrow FeO^+(C_6H_6) + h\nu \tag{5a}$$

$$FeO^+(C_6H_6) + CO \rightarrow Fe^+(C_6H_6) + CO_2 \tag{5b}$$

The net result of this catalytic cycle is the oxidation of CO to CO_2, reaction (6).

$$O + CO \rightarrow CO_2 \tag{6}$$

Should reaction (5a) produce $FeO^+ + C_6H_6$, a sequential reaction of FeO^+ with CO would produce CO_2 catalytically. Should reaction (5a) also produce $Fe^+ + C_6H_6O$, the catalytic oxidation of benzene by atomic oxygen would be the result. In the extreme of the attachment of Fe^+ to carbonaceous grains, the analogous chemistry, reactions (7a) and (7b), would resemble surface catalysis.

$$Fe^+(\text{grain}) + O \rightarrow FeO^+(\text{grain}) + h\nu \tag{7a}$$

$$FeO^+(\text{grain}) + CO \rightarrow Fe^+(\text{grain}) + CO_2 \tag{7b}$$

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